



Dehydrative esterification of carboxylic acids with alcohols catalyzed by diarylammonium *p*-dodecylbenzenesulfonates in water

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ABSTRACT

We have developed direct esterification reaction of carboxylic acids with alcohols catalyzed by diarylammonium salt catalysts toward the recovery of acetic acid from wastewater of chemical plants. Hydrophobicity of the catalysts could suppress their solubility in water. This esterification reaction has been applied to the recovery of acetic acid using a flow reaction system which is applicable to practical use in chemical plants. It was shown that this catalytic system was also applicable to the combination of hydrophobic substrates in water.

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1. Introduction

Recently, much attention has been paid to the development of environmentally benign, sustainable chemical processes. In particular, organic reactions in water are promising processes since the use of harmful organic solvents can be avoided [1–4]. We have been studied on the organic reactions in water and developed catalytic reaction systems [5,6], such as aldol [7–9], allylation [10], and Mannich-type reactions [11]. We also developed dehydration reactions in water, and found sulfonic acids which have surfactant-like structure, such as *p*-dodecylbenzenesulfonic acid (DBSA), are efficient catalysts for dehydration reactions [12] such as esterification [13,14], etherification [14], and carbon–carbon bond-forming reaction [15] in water.

On the other hand, recovery of useful organic chemicals, such as organic acids, alcohols and amino acids, from wastewater of chemical plants is desirable from a view point of green chemistry. However, recovering these organic chemicals is very difficult because concentrations of organic chemicals in drain water are usually very low. For example, distillation method needs much energy to heat and evaporate large amount of water which is not desired. At present, these wastewaters are usually treated by activated sludge. As a result of metabolism of bacteria, organic

constituents are decomposed into CO₂ or accumulated as excess activated sludge which is finally incinerated to generate CO₂. We focused on recovery of acetic acid [16–20], which is a common constituent of wastewater.

Herein we report an efficient catalytic system for direct esterification reactions [21] of carboxylic acids with alcohols in water, which enable recovery of acetic acid from its dilute aqueous solution.

2. Experimental

2.1. Material and methods

¹H and ¹³C NMR spectra are recorded on a JEOL ECX-400 spectrometer in CDCl₃ or CD₃OD. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2010 gas chromatograph with a capillary column (Agilent J&W DB-WAXetr). Dodecylbenzenesulfonic acid (soft type) was purchased from Tokyo Kasei Kogyo Co., Ltd. This is a mixture of linear alkylbenzenesulfonic acids. Its molecular weight was regarded as 326.50. *N*-octadecylbenzenamine [22], *N*-octadecyldiphenylamine [23] and di(2,4,6-trimethylphenyl)amine [24] were synthesized according to the literature. Di(4-*tert*-butylphenyl)amine was obtained from Seiko Chemical Co., Ltd., Japan. 2-Octyl-1-dodecanol (ODN) was purchased from Kao Corporation, Japan. Unless otherwise noted, other materials were obtained from commercial suppliers and used without further purification. The structures

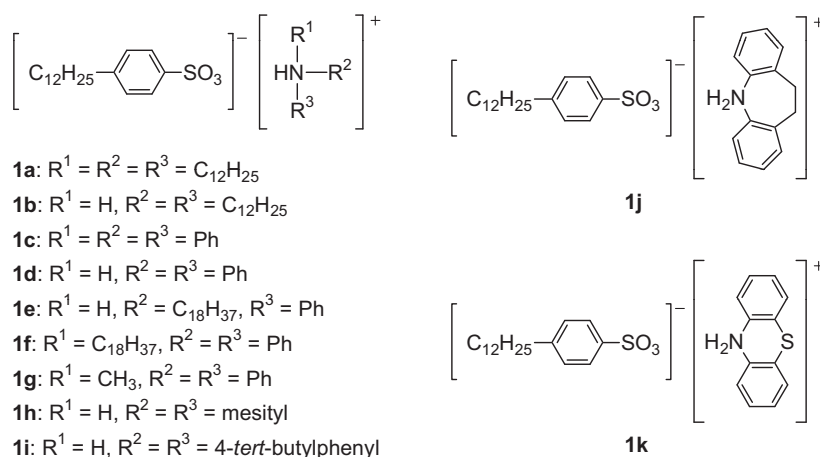
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Table 1

Reaction scheme: Acetic acid + 1-octadecanol (4 equiv.) $\xrightarrow[\text{H}_2\text{O}, 80^\circ\text{C}, 4\text{ h}]{\text{catalyst (5 mol\%)}}$ Octadecyl acetate

Entry	Catalyst	Yield (%)
1	C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ H (DBSA)	33
2	C ₁₈ H ₃₇ C ₆ H ₄ SO ₃ H	28
3	C ₁₂ H ₂₅ SO ₃ H	4
4	C ₁₆ H ₃₃ SO ₃ H	11
5	C ₈ F ₁₇ SO ₃ H	14
6	2-Naphthalenesulfonic acid	0
7	Butyl-2-naphthalenesulfonic acid	5
8	1a	0
9	1b	6
10	1c^a	30
11	1d	25
12	1e	4
13	1f	28
14	1j	34

^a Salt was not formed.**Chart 1.** Ammonium *p*-dodecylbenzenesulfonates.

of the known compounds (2-octyldodecane-1-yl acetate (ODA), 3-phenyl-1-propyl laurate, dodecyl laurate, tetradecyllaureate, tetradecyl 5-phenylvalerate, tetradecylelaidate, tetradecylcyclohexanecarboxylate) were confirmed by comparison with published data [13,25].

2.2. Preparation of ammonium *p*-dodecylbenzenesulfonate

Equimolar amount of amine and DBSA are dissolved in ~10 times volume of hexane at room temperature. The solvent was evaporated to dryness and the formation of the salt was

confirmed by ¹H NMR in CDCl₃. For example, signals of di(4-*tert*-butylphenyl)amine at 7.25 and 6.97 ppm corresponding to aromatic proton were shifted to 7.50 and 7.38 ppm, respectively and peaks of DBSA at 7.83 and 7.28 ppm were shifted to 7.59 and 7.33 ppm, respectively in the 1:1 mixture of di(4-*tert*-butylphenyl)amine and DBSA in CDCl₃ solution.

2.3. General procedure for the esterification reactions (Table 1)

A mixture of 0.2 M aqueous acetic acid solution (0.2 mmol), ODN (0.8 mmol) and catalyst (0.01 mmol) was stirred for 4 h at 80 °C.

Table 2

Reaction scheme: Acetic acid + 1-octadecanol (20 equiv.) $\xrightarrow[\text{H}_2\text{O}, 80^\circ\text{C}, 1\text{ h}]{\text{catalyst (147 mol\%)}}$ Octadecyl acetate

Entry	Catalyst	Yield (%)	Distribution ratio of catalyst ^a (organic phase/aqueous phase)
1	DBSA	59	89.2/10.8
2	1d	60	96.7/3.3
3	1f	67	98.0/2.0
4	1g	67	94.5/5.5
5	1h	64	96.9/3.1
6	1i	54	99.0/1.0
7	1j	66	97.8/2.2
8	1k	56	97.7/2.3

^a Determined by ¹H NMR analysis based on the ratio of DBSA.

Table 3
Esterification reaction in flow system.^a

Entry	Catalyst	Yield (%)	Distribution ratio of catalyst ^c (organic phase/aqueous phase)
1	DBSA	30	63/37
2	1i	24	95.7/4.3
3 ^b	1i	41	97.7/2.3

^a 1 wt% aqueous acetic acid and ODN containing 8 wt% of DBSA (or **1i** of the same molar ratio based on acetic acid) of catalyst were fed at 80 °C. The flow rate was 1.0 mL/min for both phases.

^b ODN with 4 wt% of **1i**. The flow rate was 0.33 mL/min for both phases.

^c Determined by ¹H NMR analysis based on the ratio of DBSA.

The reaction mixture was quenched with saturated aq. NaHCO₃, extracted with ether, washed with brine, dried over MgSO₄, then concentrated. Ester yields were determined by ¹H NMR in CDCl₃ based on integral ratios between the ester and ODN.

2.4. General procedure for determination of distribution ratio of catalyst after esterification reaction (Table 2)

A mixture of 1 wt% aqueous acetic acid solution (500 mg) and 8 wt% (as DBSA) catalyst solution in ODN (500 mg) was stirred for 1 h at 80 °C. Organic phase and aqueous phase were analyzed by ¹H NMR using hexamethyldisilane and sodium 3-(trimethylsilyl)-1-propanesulfonate respectively as an internal standard in CD₃OD to determine ester yield and distribution ratio of the catalyst.

2.5. General procedure for the esterification on flow system (Table 3)

A flow reaction system is designed so that the esterification reaction and the phase separation can be performed at the same time by a counter-current contact method (Fig. 2). An ODN solution containing 8 wt% (as DBSA) of catalyst and 1 wt% aqueous acetic acid solution were feed to the column (internal diameter 10 mm, effective length 300 mm) at the given flow rate respectively. The column was filled with McMahon packing (SUS316, 6 mm) and kept at 80 °C during reaction. The organic phase and aqueous phase were analyzed by GC to determine the ester yield and by ¹H NMR in CD₃OD using hexamethyldisilane and sodium 3-(trimethylsilyl)-1-propanesulfonate respectively as an internal standard to determine the distribution ratio of the catalyst.

2.6. General procedure for the esterification reactions (Table 4)

Carboxylic acid (0.25 mmol) was added to a mixture of alcohol (0.50 mmol) and catalyst (0.025 mmol, 10 mol%) in water (1.5 mL). The reaction mixture was stirred at 40 °C for 48 h, and quenched with saturated aq. NaHCO₃. The product was extracted with ether, washed with brine, dried over MgSO₄, then concentrated. Ester yields were determined by ¹H NMR in CDCl₃ based on integral ratios between ester and alcohol.

3. Results and discussion

We examined extraction of acetic acid, which is miscible with water better than with oil, to organic phase by transformation to 2-octyldodecane-1-yl acetate, which is the ester of acetic acid and 2-octyl-1-dodecanol which is a fatty alcohol (Fig. 1). Since ODN is high hydrophobic and liquid at ambient temperature, it is suitable as a reactant in this recovery system. We have envisioned that ODA is converted to a valuable substance such as ethyl acetate by

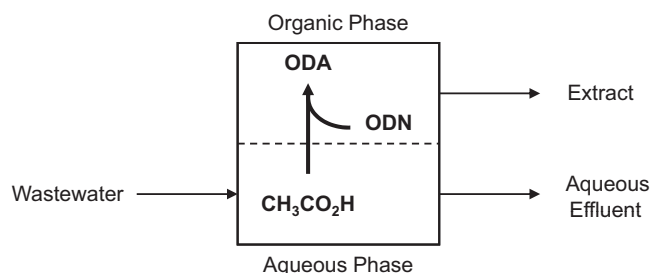


Fig. 1. A proposed system for the recovery of acetic acid from wastewater.

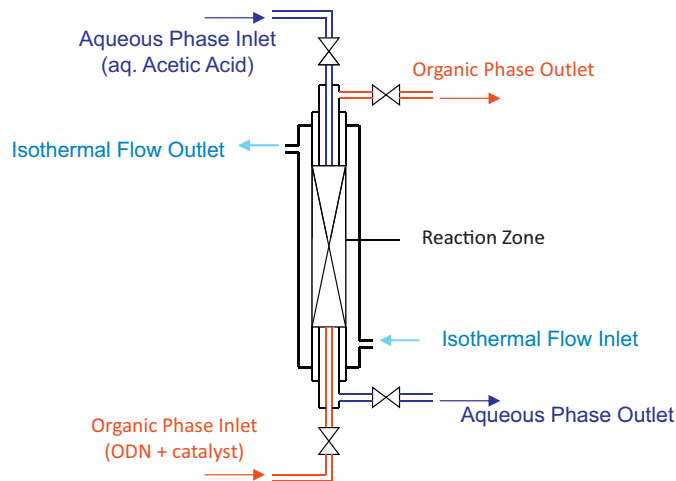


Fig. 2. A flow reaction system.

transesterification reaction and that redundant ODN is recovered and used repeatedly after the esterification reaction.

First, several sulfonic acid catalysts for the esterification reaction of acetic acid and ODN in water were examined (Table 1, entry 1–7). Among these catalysts, alkylbenzenesulfonic acid with long alkyl chains efficiently promoted the reaction (entries 1 and 2). Especially in the case of using DBSA as a catalyst, the desired ester was obtained in as much as 33% yield despite very low concentration (ca. 1.2 wt%) of acetic acid in water. However, because DBSA shows moderate solubility in water, use of DBSA in an actual wastewater treatment process is not suitable in the viewpoints of environmental effect and cost. We then examined ammonium salt catalysts [26–32] which are considered to be more hydrophobic than free sulfonic acids because of alkyl or aryl substituents on the amine (Chart 1). Various ammonium salts of DBSA were prepared and their catalytic activities were investigated (Table 1, entries 8–14). Ammonium salts of DBSA could be easily prepared by removing solvents from hexane solutions of DBSA and the corresponding amines. Triphenylamine is considered not to form a salt with DBSA in organic solvents because no peak shift was observed by NMR analysis (entry 10). Comparable yields to those using DBSA were obtained when diarylammonium salts of DBSA were employed (entries 11, 13 and 14). On the other hand, lower yields for alkyl ammonium salts (entries 8 and 9) and monoarylammonium salt (entry 12) were obtained.

We further investigated the effect of structures of diarylamine moiety on catalytic activity and distribution ratio of the catalysts (Table 2). DBSA (8 wt% of ODN, 147 mol% based on acetic acid) showed moderate yield and apparently high distribution in the aqueous phase under the conditions. Although the esterification

Table 4

$\text{RCO}_2\text{H} + \text{HOR}' \xrightarrow[\text{H}_2\text{O}]{\text{cat. (10 mol\%)}} \text{RCO}_2\text{R}'$ <p>(1 equiv.) (2 equiv.) 40 °C, 48 h</p>		Yield (%)		
R	R'	1d	1i	DBSA ^a
CH ₃ (CH ₂) ₁₀ —	—(CH ₂) ₃ Ph	93	77	89
CH ₃ (CH ₂) ₁₀ —	—(CH ₂) ₁₁ CH ₃	92	96	97
CH ₃ (CH ₂) ₁₀ —	—(CH ₂) ₁₃ CH ₃	95	91	>99
Ph(CH ₂) ₄ —	—(CH ₂) ₁₃ CH ₃	95	92	97
CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ —	—(CH ₂) ₁₃ CH ₃	96	94	97
c-Hex	—(CH ₂) ₁₃ CH ₃	92	91	95

^a Ref. [13].

yields for each diarylammonium salt catalyst were similar to that for DBSA, the distribution ratios were significantly improved. The best ratio (organic phase/aqueous phase=99.0/1.0) was obtained when the salt of DBSA and di(4-*tert*-butylphenyl)amine (**1i**) was employed (entry 6).

With a practical application to chemical plants in mind, we then applied this reaction to a flow reaction system (Fig. 2). In this system, the organic phase (ODN and catalyst) which flows upward and the aqueous phase (acetic acid and water) which flows oppositely are mixed, and the reaction proceeds in the column packed with McMahon packing. DBSA and di(4-*tert*-butylphenyl)ammonium *p*-dodecylbenzenesulfonate (**1i**) were examined as a catalyst. While the ratio of DBSA eluted to the aqueous phase was as high as 37% (entry 1), **1i** could suppress the ratio to only 4.3% under the same conditions (entry 2). After optimization of the reaction conditions, the ester yield was improved to 41% and the elution of the catalyst was suppressed to 2.3% (entry 3). These results indicate that diarylammonium *p*-dodecylbenzenesulfonate is superior to the conventional surfactant-like sulfonic acid catalysts for the application to the recovery of acetic acid from wastewaters. Since we are planning to recover ca. 50% of acetic acid from wastewater, 41% yield is within acceptable range at this stage.

Finally, we examined versatility of the diarylammonium salt catalysts for other esterification reactions (Table 4). In most cases using **1d** (diphenylamine salt) or **1i**, high yields were obtained under the conditions although DBSA gave slightly dominant yields. These results show the catalytic system using diarylammonium *p*-dodecylbenzenesulfonates is applicable not only to hydrophilic substrates but also to hydrophobic substrates in water.

4. Conclusion

We have developed the direct esterification reaction of carboxylic acids with alcohols catalyzed by diarylammonium salt catalysts. This esterification reaction could be applied to the recovery of acetic acid in the flow reaction system which is applicable to practical use in the chemical plant. This catalytic system is also applicable to the combination of hydrophobic substrates in water. Further investigations focused on the application to the actual wastewater treatment are now in progress.

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